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The main objective of this research, performed by Sven E. Eklund, a graduate student at the Univ of Tennessee, Knoxville, is to explore the fundamentals of electroplating of several refractory metals, such as tungsten and tantalum, from chlorofluoroaluminate melts and to compare with electroplating of these elements from the LiF-NaF-KF eutectic. There has been considerable interest in the electrochemistry and metallurgy of the Groups IV-B, V-B, and VI-B transition metals (so-called refractory metals) because of the potential use of these metals in electronic components, electrical devices, and the aerospace industry. Pure, coherent deposits of these metals were originally obtained by a method developed by Mellors and Senderoff [1] in 1965. This method uses electrolytic reduction to the metal from the ternary eutectic LiF-NaF-KF, or FLINAK. Mechanisms proposed in several articles by Senderoff and coworkers for the reduction of several metals [2-5] have spurred research into the refractory metals in molten fluorides.

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Electroplating of Refractory Metals Using Haloaluminate Melts.

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Gleb Mamantov  
Principal Investigator

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The main objective of this research, performed by Sven E. Eklund, a graduate student at the University of Tennessee, Knoxville, is to explore the fundamentals of electroplating of several refractory metals, such as tungsten and tantalum, from chlorofluoroaluminate melts and to compare with electroplating of these elements from the LiF-NaF-KF eutectic.

There has been considerable interest in the electrochemistry and metallurgy of the Groups IV-B, V-B, and VI-B transition metals (so-called refractory metals) because of the potential use of these metals in electronic components, electrical devices, and the aerospace industry. Pure, coherent deposits of these metals were originally obtained by a method developed by Mellors and Senderoff[1] in 1965. This method uses electrolytic reduction to the metal from the ternary eutectic LiF-NaF-KF, or FLINAK. Mechanisms proposed in several articles by Senderoff and coworkers for the reduction of several metals [2-5] have spurred research into the refractory metals in molten fluorides.

Most of our studies of refractory metals have been performed in alkali chloroaluminates. By comparison with FLINAK, sodium chloroaluminate ( $\text{AlCl}_3$ -NaCl) melts may be considered as favorable systems in several respects. First, the liquidus temperatures for chloroaluminates lie below 200°C for melt compositions in the range from 49.8 to 100 mole percent  $\text{AlCl}_3$ , while FLINAK has a eutectic point of 454°C, and generally temperatures in excess of 750°C are required for refractory metal deposition. The Lewis melt acidity can be varied over a broad range by changing the  $\text{AlCl}_3$  to NaCl ratio. Finally, the highly aggressive nature of fluoride melts and the temperatures required for their use greatly limit the materials which can be used for bath construction, whereas chloroaluminate studies can be conducted using even simple Pyrex cells.

Studies of the reduction of tantalum (V) [6], niobium (V) [7], and tungsten (VI) [8], in acidic ( $\text{AlCl}_3$ -rich) alkali chloroaluminates show that low oxidation state cluster species, such as  $\text{Ta}_6\text{Cl}_{14}$  and  $\text{W}_6\text{Cl}_{12}$ , are formed which, due to high stability and/or insolubility in the melt, prevent further reduction to the metal. In basic (usually  $\text{AlCl}_3$ -NaCl<sub>sat</sub>) melts, problems can arise because of small amounts of oxide-containing species. This contamination by oxides, arising either from atmospheric impurities or attack of Pyrex by the melt, can be greatly reduced by passing phosgene or carbon tetrachloride through the melt [9,10].

Fluoride-containing chloroaluminate melts are a possible compromise between the use of fluoride melts, which require somewhat severe conditions, and low-temperature chloroaluminate melts. It was felt initially that the inclusion of fluoride into the chloroaluminate melts may sufficiently inhibit the formation of cluster species as to allow reduction to the metal.

Recently we have extended our studies of selected refractory metals, specifically niobium, tantalum and tungsten, to basic  $\text{AlCl}_3$ - $\text{NaCl}$  which has been treated with  $\text{COCl}_2$  to remove oxide impurities. The electrochemistry of these elements is being studied as a function of temperature. Also, the electrochemistry in basic chloroaluminates is being compared with that observed in sodium fluorochloroaluminates or NAFCAL. We have determined that all three elements can be deposited from either basic  $\text{NaAlCl}_4$  or NAFCAL at temperatures lower than those required for deposition from FLINAK (600 to 650°C compared to 750°C for FLINAK). Further studies are needed to determine the quality of the deposit (or plate). We have also conducted plating of Ta and Nb from FLINAK; the plates appear to be comparable to those reported by Senderoff and Mellors[5] although significant electrochemical differences with those of Senderoff and Mellors were observed.

The reduction of Ta(V) in  $\text{AlCl}_3$ - $\text{NaCl}_{\text{sat}}$  melts containing 10 mole % NaF was investigated by voltammetric and spectroscopic methods, and exhaustive electrolysis at 200-450°C (11). The reduction to Ta metal proceeds through the formation of Ta(IV), Ta(III), and Ta(II). The species involving Ta(III) and Ta(II) are very unstable forming clusters  $\text{Ta}_6\text{Cl}_{12}^{3+}$  and  $\text{Ta}_6\text{Cl}_{12}^{2+}$  which are slowly reduced to metallic tantalum.

The reduction of Nb(V) in  $\text{AlCl}_3$ - $\text{NaCl}_{\text{sat}}$  melts at 180°C also involves the formation of Nb(IV) and cluster species  $\text{Nb}_3^{3+}$  and  $\text{Nb}_6^{15+}$ ; temperatures >525°C were needed for the deposition of Nb metal (12). Additions of NaF had little, if any, effect on the nature of the deposit formed.

The reduction of W(V) in  $\text{AlCl}_3$ - $\text{NaCl}_{\text{sat}}$  was studied to determine the effect of oxide (13); these studies are continuing.

The current studies utilize a vacuum tight quartz cell which contains a glassy carbon crucible containing the melt. Initial experiments have been conducted with FLINAK as the solvent; the components of FLINAK ( $\text{LiF}$ ,  $\text{NaF}$ ,  $\text{KF}$ ) were recrystallized to minimize oxide content (14).

Initially, the cyclic voltammetry of Ta(V) (added as  $\text{K}_2\text{TaF}_7$ ) in FLINAK was briefly explored; three reduction waves were observed. Currently we are examining the electrochemical behavior of tungsten in FLINAK. The compound  $\text{WF}_4$  was synthesized to be used as the solute; however, it was learned that  $\text{WF}_4$  decomposes above 300°C. We are now adding gaseous  $\text{WF}_6$  to FLINAK containing metallic tungsten; according to Mellors and Senderoff(15) this approach results in an intermediate oxidation state of tungsten which we plan to characterize by spectroscopic methods.

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